

IN THE CLAIMS

1. (Previously presented) A method for preparing a cycloolefin polymer containing polar functional groups, comprising:

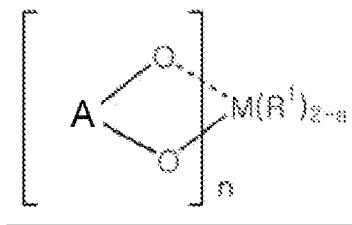
a) preparing a catalyst mixture including

i) a precatalyst represented by Chemical Formula 1, containing a Group 10 transition metal having a ligand containing oxygen ions bonded to the metal;

ii) a first cocatalyst which is an organic compound containing a Group 15 element; and

iii) a second cocatalyst which is capable of providing an anion and weakly coordinating to the metal of the precatalyst; and

b) subjecting a monomer solution comprising a norbornene-based compound having an exo isomer content of more than 50 mol%, containing a polar functional group, and represented by the following Chemical Formula 5, to an addition polymerization reaction in the presence of an organic solvent and the catalyst mixture, at a temperature of 80-200 °C, the total amount of the organic solvent being 50-800 % by weight based on the total weight of the monomer contained in the monomer solution, and the product yield of the cycloolefin polymer being 50% by weight or more based on the total weight of the monomer wherein the polymer comprises more than 30 mol% of norbornene-based compound containing a polar functional group represented by the following Chemical Formula 5:

Chemical Formula 1

wherein

M is a Group 10 transition metal;

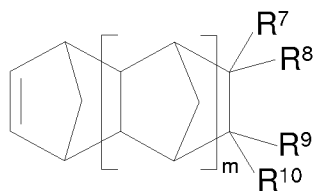
n is 1 or 2;

A represents a linear or branched C₁₋₂₀ alkylene, arylene, aralkylene, or

alkenylene group or a linear or branched C₁₋₂₀ alkylene, arylene, aralkylene, or alkenylene group containing a hetero atom including Si, Ge, S, O, or N;

R¹ is hydrogen; a linear or branched C₁₋₂₀ alkyl, alkenyl or vinyl group; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted with a hydrocarbon; a C₆₋₄₀ aryl group unsubstituted or substituted with a hydrocarbon; a C₆₋₄₀ aryl group containing at least one hetero atom; a C₇₋₁₅ aralkyl group unsubstituted or substituted with a hydrocarbon; or a C₃₋₂₀ alkynyl group;

Chemical Formula 5



wherein

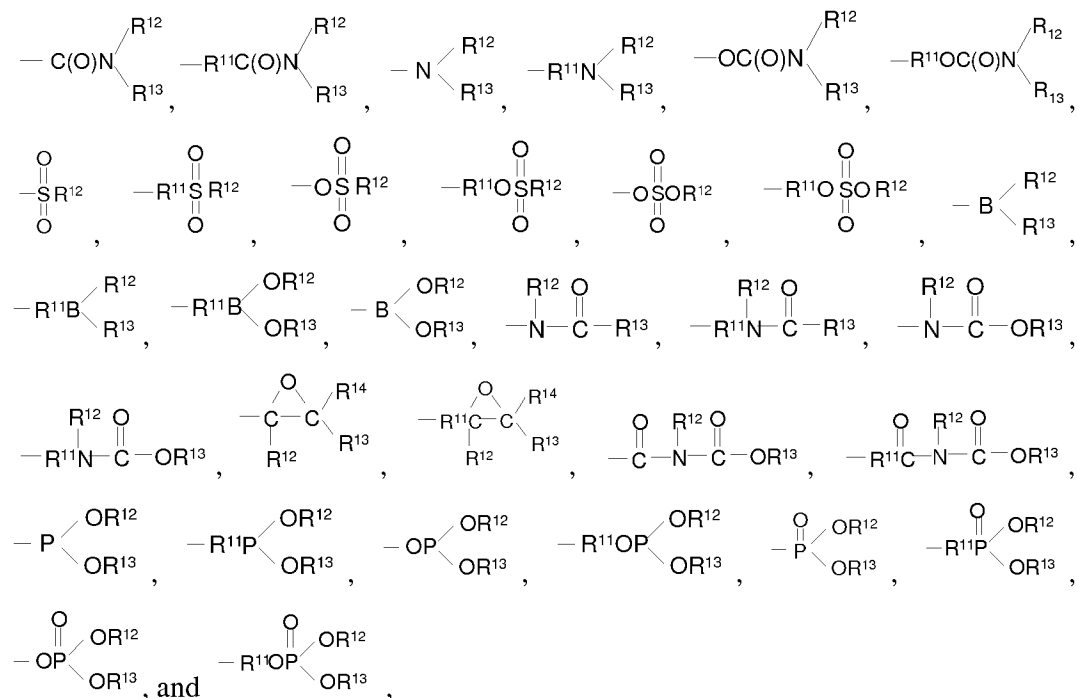
m is an integer of 0 to 4,

at least one of R⁷, R⁸, R⁹ and R¹⁰ is a polar functional group, the others are non-polar functional group, and R⁷, R⁸, R⁹ and R¹⁰ can be bonded together to form a saturated or unsaturated C₁₋₂₀ cyclic group or C₆₋₂₄ aromatic ring;

the non-polar functional group includes hydrogen; halogen; a linear or branched C₁₋₂₀ alkyl group; a linear or branched C₁₋₂₀ haloalkyl group; a linear or branched C₁₋₂₀ alkenyl group; a linear or branched C₁₋₂₀ haloalkenyl group; a linear or branched C₃₋₂₀ alkynyl group; a linear or branched C₃₋₂₀ haloalkynyl; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C₆₋₄₀ aryl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; and a C₇₋₁₅ aralkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl;

the polar functional group is a non-hydrocarbonaceous polar group containing at least one of O, N, P, S, Si and B, and is selected from the group consisting of: OR¹², OC(O)OR¹², R¹¹OC(O)OR¹², C(O)R¹², R¹¹C(O)R¹², OC(O)R¹², R¹¹OC(O)R¹², (R¹¹O)pOR¹², (OR¹¹)pOR¹², C(O)OC(O)R¹², R¹¹C(O)OC(O)R¹², SR¹², R¹¹SR¹², SSR¹²,

$R^{11}SSR^{12}$, $S(=O)R^{12}$, $R^{11}S(=O)R^{12}$, $R^{11}C(=S)R^{12}$, $R^{11}C(=S)SR^{12}$, $R^{11}SO_3R^{12}$, SO_3R^{12} ,
 $R^{11}N=C=S$, NCO , $R^{11}NCO$, CN , $R^{11}CN$, $NNC(=S)R^{12}$, $R^{11}NNC(=S)R^{12}$, NO_2 , $R^{11}NO_2$,



in which R^{11} is a linear or branched C_{1-20} alkyl group; a linear or branched C_{1-20} haloalkyl group; a linear or branched C_{1-20} alkenyl group; a linear or branched C_{1-20} haloalkenyl group; a linear or branched C_{3-20} alkynyl group; a linear or branched C_{3-20} haloalkynyl; a C_{3-12} cycloalkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C_{6-40} aryl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; and a C_{7-15} aralkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl;

R^{12} , R^{13} , and R^{14} are each independently hydrogen; a halogen; a linear or branched C_{1-20} alkyl group; a linear or branched C_{1-20} haloalkyl group; a linear or branched C_{1-20} alkenyl group; a linear or branched C_{1-20} haloalkenyl group; a linear or branched C_{3-20} alkynyl group; a linear or branched C_{3-20} haloalkynyl; a C_{3-12} cycloalkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C_{6-40} aryl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C_{7-15} aralkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl;

or haloalkynyl; or alkoxy, haloalkoxy, carbonyloxy, halocarbonyloxy; and
p is an integer of 1 to 10.

2. to 5. (Canceled)

6. (Original) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the organic solvent is selected from the group consisting of dichloromethane, dichloroethane, toluene, chlorobenzene and mixtures thereof.

7. (Canceled)

8. (Original) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the total amount of the organic solvent is 50-200 % by weight based on the total weight of the monomer contained in the monomer solution.

9. (Canceled)

10. (Original) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the polymerization reaction is performed at a temperature of 80-150°C.

11. (Original) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the catalyst mixture includes a metal catalyst complex containing a cation complex made of the precatalyst and the first cocatalyst and an anion complex made of the second cocatalyst.

12. (Previously Presented) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the catalyst mixture comprises, based on 1 mole of the precatalyst, 1-3 moles of the first cocatalyst; and 1-2 moles of the second cocatalyst.

13. (Original) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the molar ratio of the catalyst mixture based on the precatalyst to the monomer contained in the monomer solution is in the range of 1:2,500 - 1:100,000.

14. and 15. (Canceled).

16. (Original) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the monomer solution further comprises a cycloolefin compound containing no polar functional group.

17. (Original) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 16, wherein the molar ratio of the cycloolefin compound containing no polar functional group is 30 % by mole based on the total monomers contained in the monomer solution.

18. (Previously presented) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the cycloolefin polymer containing polar functional groups includes a homopolymer of a cycloolefin monomer containing a polar functional group, a copolymer of cycloolefin monomers containing different polar functional groups, and a copolymer of cycloolefin monomers containing a polar functional group and cycloolefin monomers containing no polar functional group.

19. (Original) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein a molecular weight (Mw) of the cycloolefin polymer containing polar functional groups is in the range of 100,000-

1,000,000.

20. to 24. (Canceled).

25. (Previously presented) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein i) the precatalyst is selected from the group consisting of an $\text{Pd}(\text{acetyl acetate})_2$, $\text{Pd}(\text{acetate})_2$, and $(\text{acetate})\text{Pd}(\text{acetyl acetate})$.

26. (Previously presented) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 35, wherein ii) the first cocatalyst is tricyclohexylphosphine.

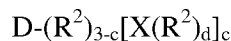
27. (Previously presented) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 36, wherein iii) the second cocatalyst is dimethyl aniliniumtetrakis(pentafluorophenyl)borate.

28. (Previously presented) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 37, wherein the norbornene-based compound contains a polar functional group selected from the group consisting of 5-norbornene-2-carboxylic acid methyl ester, 5-norbornene-2-carboxylic acid butyl ester, 5-norbornene-2-allylacetate, 5-norbornene-2-acetate.

29. to 34. (Canceled)

35. (Previously presented) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the organic compound of the first cocatalyst has an unshared electron pair and serves as an electron donor and is represented by Chemical Formula 2 or Chemical Formula 3:

Chemical Formula 2



wherein

D is a Group 15 element,

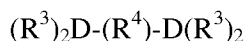
c is an integer of 0 to 3,

X is an oxygen, sulfur, nitrogen or silicon,

d is 1 when X is an oxygen or sulfur, 2 when X is a nitrogen atom, or 3 when X is a silicon,

R^2 is hydrogen; a linear or branched C_{1-20} alkyl, alkoxy, allyl, alkenyl or vinyl group; a C_{3-12} cycloalkyl group unsubstituted or substituted with a hydrocarbon; a C_{6-40} aryl group unsubstituted or substituted with a hydrocarbon; a C_{7-15} aralkyl group unsubstituted or substituted with a hydrocarbon; a C_{3-20} alkynyl group; a tri(linear or branched C_{1-10} alkyl) silyl or tri(linear or branched C_{1-10} alkoxy) silyl group; a tri(C_{3-12} cycloalkyl unsubstituted or substituted with a hydrocarbon) silyl group; a tri(C_{6-40} aryl unsubstituted or substituted with a hydrocarbon) silyl group; a tri(C_{6-40} aryloxy unsubstituted or substituted with a hydrocarbon) silyl group; a tri(linear or branched C_{1-10} alkyl) siloxy group; a tri(C_{3-12} cycloalkyl unsubstituted or substituted with a hydrocarbon) siloxy group; or tri(C_{6-40} aryl unsubstituted or substituted with a hydrocarbon) siloxy group, in which all these substituents may be substituted with a linear or branched haloalkyl group or a halogen;

Chemical Formula 3



wherein

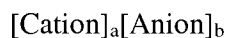
D is a Group 15 element,

R^3 is as defined in R^2 of Chemical Formula 3;

R^4 is a linear or branched C_{1-5} alkyl, alkenyl or vinyl group; a C_{3-12} cycloalkyl group unsubstituted or substituted with a hydrocarbon; a C_{6-20} aryl group unsubstituted or substituted with a hydrocarbon; or a C_{7-15} aralkyl group unsubstituted or substituted with a hydrocarbon.

36. (Previously presented) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the second cocatalyst is a salt represented by Chemical Formula 4:

Chemical Formula 4



wherein

Cation is selected from the group consisting of proton; cations of Group 1 and 2 metals; and organic groups containing these cations, to which unshared electron pairs of the organic compound of the first catalyst may be bonded;

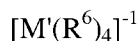
Anion is an anion capable of weakly coordinating to the metal M of the precatalyst, and is selected from the group consisting of borate anion, aluminate anion, $[\text{SbF}_6]^{-1}$, $[\text{PF}_6]^{-1}$, $[\text{AsF}_6]^{-1}$, perfluoroacetate anion ($[\text{CF}_3\text{CO}_2]^{-1}$), perfluoropropionate anion ($[\text{C}_2\text{F}_5\text{CO}_2]^{-1}$), perfluorobutyrate anion ($[\text{CF}_3\text{CF}_2\text{CF}_2\text{CO}_2]^{-1}$), perchlorate anion ($[\text{ClO}_4]^{-1}$), p-toluenesulfonate anion ($[\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3]^{-1}$), $[\text{SO}_3\text{CF}_3]^{-1}$, boratabenzene anion, and carborane anion unsubstituted or substituted with a halogen atom; and

a and b are the number of the cations and anions, respectively, and determined to allow the cation and anion to be electrically neutralized and balance the charges.

37. (Previously presented) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 36, wherein the organic group containing the cation of Chemical Formula 4 is selected from the group consisting of ammoniums $[\text{NH}(\text{R}^5)_3]^+$, $[\text{NH}_2(\text{R}^5)_2]^+$, $[\text{NH}_3(\text{R}^5)_1]^+$, and $[\text{N}(\text{R}^5)_4]^+$; phosphoniums $[\text{PH}(\text{R}^5)_3]^+$, $[\text{PH}_2(\text{R}^5)_2]^+$, $[\text{PH}_3(\text{R}^5)_1]^+$, and $[\text{P}(\text{R}^5)_4]^+$; carboniums $[\text{C}(\text{R}^5)_3]^+$; $[\text{H}(\text{OEt}_2)_2]^+$; and $[\text{Cp}_2\text{Fe}]^+$, in which R^5 is a linear or branched C_{1-20} alkyl group; an alkyl or silylalkyl group substituted with a halogen; a C_{3-12} cycloalkyl group unsubstituted or substituted with a hydrocarbon; a cycloalkyl or silyl cycloalkyl group substituted with a halogen; a C_{6-40} aryl group unsubstituted or substituted with a hydrocarbon; an aryl or silyl aryl group substituted with a halogen; a C_{7-15} aralkyl group unsubstituted or substituted with a hydrocarbon; or an aralkyl or silyl aralkyl group substituted with a halogen.

38. (Previously presented) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 36, wherein the borate anion or aluminate anion of Chemical Formula 4 is an anion represented by Chemical Formula 4a or 4b:

Chemical Formula 4a



Chemical Formula 4b



wherein

M' is a boron or aluminum;

R^6 is a halogen; a linear or branched C_{1-20} alkyl or alkenyl group unsubstituted or substituted with a halogen atom; a C_{3-12} cycloalkyl group unsubstituted or substituted with a halogen; a C_{6-40} aryl group which unsubstituted or substituted with a halogen or hydrocarbon; a C_{6-40} aryl group substituted with a linear or branched C_{3-20} trialkylsiloxy group or a linear or branched C_{18-48} triarylsiloxy group; or a C_{7-15} aralkyl group unsubstituted or substituted with a halogen.

39. (Previously presented) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the polar functional group of the norbornene-based compound includes an ester group and an acetyl group.

40. (Canceled).

41. (Previously presented) A method for preparing a cycloolefin polymer containing polar functional groups, comprising:

a) preparing a catalyst mixture including

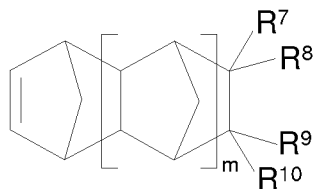
i) a precatalyst selected from the group consisting of (allyl)Pd(acetyl acetonate), (allyl)Pd(acetate), (acetate)Pd(acetyl acetonate), and a mixture thereof;

ii) a first cocatalyst which is an organic compound containing a Group 15 element; and

iii) a second cocatalyst which is capable of providing an anion and weakly coordinating to the metal of the precatalyst; and

b) subjecting a monomer solution comprising a norbornene-based compound containing a polar functional group and represented by the following Chemical Formula 5 to an addition polymerization reaction in the presence of an organic solvent and the catalyst mixture, at a temperature of 80-200 °C, the total amount of the organic solvent being 50-800 % by weight based on the total weight of the monomer contained in the monomer solution, and the product yield of the cycloolefin polymer being 50% by weight or more based on the total weight of the monomer, wherein the polymer comprises more than 20 mol% of norbornene-based compound containing a polar functional group represented by the following Chemical Formula 5:

Chemical Formula 5



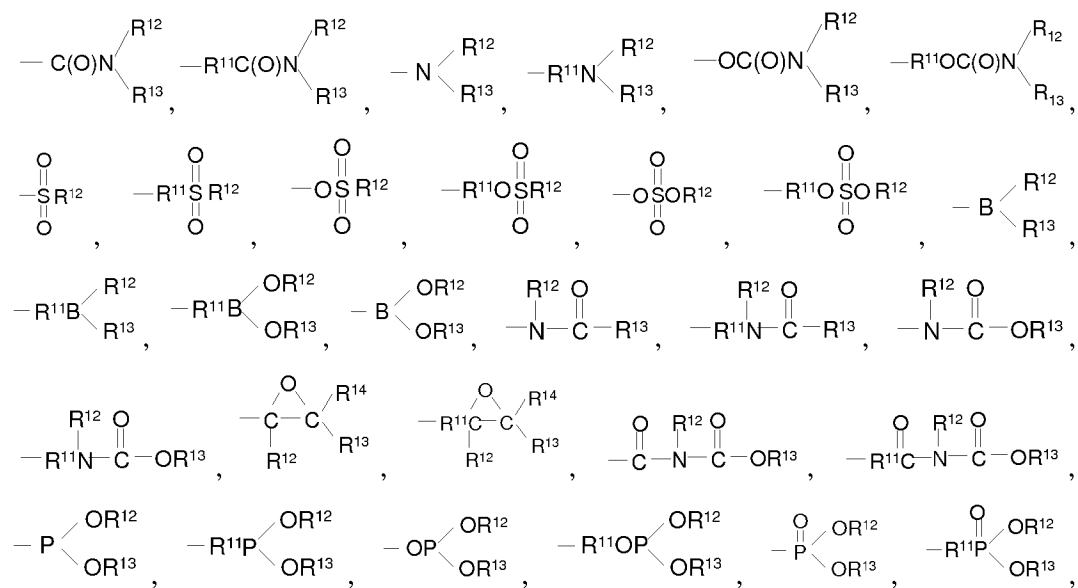
wherein

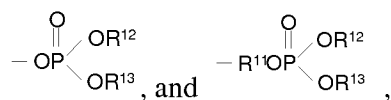
m is an integer of 0 to 4,

at least one of R^7 , R^8 , R^9 and R^{10} is a polar functional group, the others are non-polar functional group, and R^7 , R^8 , R^9 and R^{10} can be bonded together to form a saturated or unsaturated C_{1-20} cyclic group or C_{6-24} aromatic ring;

the non-polar functional group includes hydrogen; halogen; a linear or branched C_{1-20} alkyl group; a linear or branched C_{1-20} haloalkyl group; a linear or branched C_{1-20} alkenyl group; a linear or branched C_{1-20} haloalkenyl group; a linear or branched C_{3-20} alkynyl group; a linear or branched C_{3-20} haloalkynyl; a C_{3-12} cycloalkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C_{6-40} aryl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; and a C_{7-15} aralkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl;

the polar functional group is a non-hydrocarbonaceous polar group containing at least one of O, N, P, S, Si and B, and is selected from the group consisting of: OR^{12} , $OC(O)OR^{12}$, $R^{11}OC(O)OR^{12}$, $C(O)R^{12}$, $R^{11}C(O)R^{12}$, $OC(O)R^{12}$, $R^{11}OC(O)R^{12}$, $(R^{11}O)pOR^{12}$, $(OR^{11})pOR^{12}$, $C(O)OC(O)R^{12}$, $R^{11}C(O)OC(O)R^{12}$, SR^{12} , $R^{11}SR^{12}$, SSR^{12} , $R^{11}SSR^{12}$, $S(=O)R^{12}$, $R^{11}S(=O)R^{12}$, $R^{11}C(=S)R^{12}$, $R^{11}C(=S)SR^{12}$, $R^{11}SO_3R^{12}$, SO_3R^{12} , $R^{11}N=C=S$, NCO , $R^{11}NCO$, CN , $R^{11}CN$, $NNC(=S)R^{12}$, $R^{11}NNC(=S)R^{12}$, NO_2 , $R^{11}NO_2$,





in which R^{11} is a linear or branched C_{1-20} alkyl group; a linear or branched C_{1-20} haloalkyl group; a linear or branched C_{1-20} alkenyl group; a linear or branched C_{1-20} haloalkenyl group; a linear or branched C_{3-20} alkynyl group; a linear or branched C_{3-20} haloalkynyl; a C_{3-12} cycloalkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C_{6-40} aryl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; and a C_{7-15} aralkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl;

R^{12} , R^{13} , and R^{14} are each independently hydrogen; a halogen; a linear or branched C_{1-20} alkyl group; a linear or branched C_{1-20} haloalkyl group; a linear or branched C_{1-20} alkenyl group; a linear or branched C_{1-20} haloalkenyl group; a linear or branched C_{3-20} alkynyl group; a linear or branched C_{3-20} haloalkynyl; a C_{3-12} cycloalkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C_{6-40} aryl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C_{7-15} aralkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; or alkoxy, haloalkoxy, carbonyloxy, halocarbonyloxy; and

p is an integer of 1 to 10.

42. (Previously presented) The method for preparing a cycloolefin polymer containing polar functional groups according to claim 41, wherein the second cocatalyst is a salt represented by Chemical Formula 4:

Chemical Formula 4



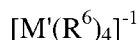
wherein

Cation is an organic group, to which unshared electron pairs of the organic compound of the first catalyst may be bonded, wherein the organic group containing the cation of Chemical Formula 4 is selected from the group consisting of ammoniums $[\text{NH}(\text{R}^5)_3]^+$, $[\text{NH}_2(\text{R}^5)_2]^+$, $[\text{NH}_3(\text{R}^5)_1]^+$, and $[\text{N}(\text{R}^5)_4]^+$; phosphoniums $[\text{PH}(\text{R}^5)_3]^+$, $[\text{PH}_2(\text{R}^5)_2]^+$, $[\text{PH}_3(\text{R}^5)_1]^+$, and $[\text{P}(\text{R}^5)_4]^+$; carboniums $[\text{C}(\text{R}^5)_3]^+$; $[\text{H}(\text{OEt}_2)_2]^+$; and $[\text{Cp}_2\text{Fe}]^+$, in which R^5 is a linear or branched C_{1-20} alkyl group; an alkyl or silylalkyl group substituted with a halogen; a C_{3-12} cycloalkyl group unsubstituted or substituted with a hydrocarbon; a cycloalkyl or silyl cycloalkyl group substituted with a halogen; a C_{6-40} aryl group unsubstituted or substituted with a hydrocarbon; an aryl or silyl aryl group substituted with a halogen; a C_{7-15} aralkyl group unsubstituted or substituted with a hydrocarbon; or an aralkyl or silyl aralkyl group substituted with a halogen;

Anion is an anion capable of weakly coordinating to the metal M of the precatalyst, and is selected from the group consisting of borate anion, aluminate anion, $[\text{SbF}_6]^{-1}$, $[\text{PF}_6]^{-1}$, $[\text{AsF}_6]^{-1}$, perfluoroacetate anion ($[\text{CF}_3\text{CO}_2]^{-1}$), perfluoropropionate anion ($[\text{C}_2\text{F}_5\text{CO}_2]^{-1}$), perfluorobutyrate anion ($[\text{CF}_3\text{CF}_2\text{CF}_2\text{CO}_2]^{-1}$), perchlorate anion ($[\text{ClO}_4]^{-1}$), p-toluenesulfonate anion ($[\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3]^{-1}$), $[\text{SO}_3\text{CF}_3]^{-1}$, boratabenzene anion, and carborane anion unsubstituted or substituted with a halogen atom; a and b are the number of the cations and anions, respectively, and determined to allow the cation and anion to be electrically neutralized and balance the charges; and

wherein the borate or aluminate of Chemical Formula 4 is an anion represented by Chemical Formula 4a or 4b:

Chemical Formula 4a



Chemical Formula 4b

wherein

M' is a boron or aluminum;

R⁶ is a halogen; a linear or branched C₁₋₂₀ alkyl or alkenyl group unsubstituted or substituted with a halogen atom; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted with a halogen; a C₆₋₄₀ aryl group which is unsubstituted or substituted with a halogen or hydrocarbon; a C₆₋₄₀ aryl group substituted with a linear or branched C₃₋₂₀ trialkylsiloxyl group or a linear or branched C₁₈₋₄₈ triarylsiloxyl group; or a C₇₋₁₅ aralkyl group unsubstituted or substituted with a halogen.